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Removal of Organic Contaminants from Groundwater: Status of EPA (Environmental Protection Agency) Drinking Water Research Program

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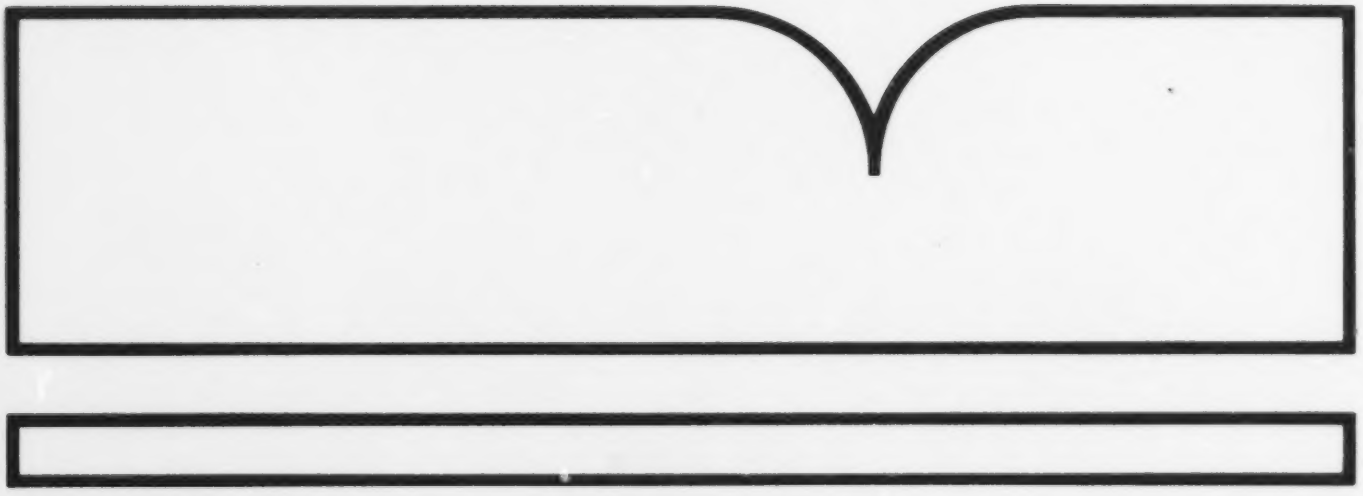

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REMOVAL OF ORGANIC CONTAMINANTS FROM GROUNDWATER: STATUS OF EPA DRINKING WATER RESEARCH PROGRAM

by

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16. ABSTRACT Groundwater is a natural resource of enormous value. Three-quarters of U.S. cities get their water supplies totally or in part from groundwater and more than half of all Americans rely on it for drinking water. Ninety percent of rural households have no source other than groundwater for drinking water supplies.

A number of recent studies have documented the actual or potential contamination of our nation's groundwater on a wide scale. A survey conducted by the U.S. Environmental Protection Agency (EPA) has documented that 22 percent of approximately 446 randomly sampled utilities produced drinking water containing volatile organic chemical (VOC's) at detectable levels. Other individual studies have shown the presence of pesticides in groundwater, and in recent years concern has been growing over contamination of groundwater by agricultural chemicals (fertilizers, insecticides, nematocides, and fungicides.

Recently, EPA has proposed maximum contaminant levels (MCL's) for VOC's (Phase I) that are frequently found in groundwater supplies. These MCL's are expected to be in final form by the fall of 1986. In addition, EPA is planning to propose 26 synthetic organic chemical MCL's (Phase II) for contaminants that are also frequently found in groundwater. Previous experience indicates that these Phase I and II regulations will have a significant impact on many water utilities in the United States.

The purpose of this paper is to discuss the status of DWRD's research activities and to provide a state-of-the-art summary on the removal of organic contaminants from groundwater.

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REMOVAL OF ORGANIC CONTAMINANTS FROM GROUNDWATER: STATUS OF EPA DRINKING WATER RESEARCH PROGRAM

by

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INTRODUCTION

Groundwater is a natural resource of enormous value. Three-quarters of U.S. cities get their water supplies totally or in part from groundwater and more than half of all Americans rely on it for drinking water. Ninety percent of rural households have no source other than groundwater for drinking water supplies.

A number of recent studies have documented the actual or potential contamination of our nation's groundwater on a wide scale. A survey conducted by the U.S. Environmental Protection Agency (EPA) has documented that 22 percent of approximately 466 randomly sampled utilities produced drinking water containing volatile organic chemicals (VOC's) at detectable levels.[1] Other individual studies have shown the presence of pesticides in groundwater, and in recent years concern has been growing over contamination of groundwater by agricultural chemicals (fertilizers, insecticides, nematocides, and fungicides). The concern is greater, of course, when specific chemicals are identified in homeowners' drinking water wells.

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Though concern in the past 5 years has centered on VOC contamination of groundwater, several examples illustrate the growing concern over pesticides. Over the last 8 years, New York's Suffolk County Health Department has examined the groundwater underlying Long Island for agricultural organic constituents and their decay products.[2] During the testing, 101 agricultural/organic compounds were evaluated, with 41 found in the groundwater. Many of these identified contaminants were present in trace quantities, but aldicarb, carbofuran, 1,2-dichloropropane, and 1,2,3-trichloropropane were at elevated levels. In addition, nitrates from fertilizer applications were present in quantities exceeding the primary drinking water standards. A 1983 study, conducted by the California Department of Food and Agriculture (1983), stated that dibromochloropropane (DBCP), ethylene dibromide (EDB), and simazine were found in San Joaquin Valley wells[3]. A report submitted to the California State Water Resources Board states that more than 2000 wells statewide have been found to be contaminated with DBCP.[3]

Work conducted near Tiffin, Ohio by EPA's Drinking Water Research Division (DWRD) has shown periodic high quantities of pesticides in surface waters associated with seasonal runoffs.[4] Although groundwaters have not been sampled in this area, it is likely that some contamination exists. Unlike surface waters, groundwaters are likely to remain contaminated indefinitely. EPA is now proposing to conduct an extensive groundwater survey for pesticides similar to the earlier VOC survey.[5]

Recently, EPA has proposed maximum contaminant levels (MCL's) for VOC's (Phase I) that are frequently found in groundwater supplies.[6] These MCL's are expected to be in final form by the fall of 1986. In addition, EPA is

planning to propose 26 synthetic organic chemical MCL's (Phase II) for contaminants that are also frequently found in groundwater.[7] Previous experience indicates that these Phase I and II regulations will have a significant impact on many water utilities in the United States.

Although the most desirable way of controlling groundwater contamination is to prevent pollution at the source, many aquifers are currently contaminated and provide the cheapest water supply to the communities they serve. Water from these aquifers can be treated to achieve quality levels that equal or exceed those being proposed by the Office of Drinking Water. EPA's Drinking Water Research Division (DWRD) has been conducting extensive research for a number of years into the development of treatment technologies for removing both inorganic and organic contaminants from groundwater in a cost-effective manner. Recently, this effort has emphasized the removal of volatile organic chemicals and synthetic organic chemicals such as pesticides.

DWRD's research activities are categorized as pilot-, bench-, and field-scale studies. Most of the bench- and pilot-scale studies are conducted on an in-house basis and are designed to examine the feasibility of various technologies before their cost and performance are evaluated in the field.

The purpose of this paper is to discuss the status of DWRD's research activities and to provide a state-of-the-art summary on the removal of organic contaminants from groundwater.

DWRD'S RESEARCH ACTIVITIES

DWRD is part of the Water Engineering Research Laboratory of the Office of Environmental Engineering and Technology in EPA's Office of Research and

Development. The division consists of 44 permanent full-time employees and has an annual budget of $5 million. DWRD is responsible for evaluating the various types of technologies that may be feasible for meeting the MCL's promulgated under the Safe Drinking Water Act (PL93-523). The standard research protocol followed by DWRD is to evaluate unit processes at the bench level, move the process to pilot scale for testing, and if its performance is promising, build a prototype for field evaluation. At all stages, cost and performance are key factors in moving a technology to the next phase. Thus when a technology is tested on a field scale, cost and performance data are routinely collected.

Table 1 summarizes the treatment technologies that DWRD is evaluating for removal of VOC's and synthetic organic chemicals (SOC's) from water supplies. The table indicates carbon adsorption is effective for removing both VOC's and SOC's. Packed tower and diffused aeration are best suited for removing VOC's. Of the technologies that show promise and are being tested at the bench- and pilot- scales, conventional treatment is effective for removing a few of the SOC's, ozone oxidation is effective for removing certain classes of volatile organic chemicals and SOC's, and certain reverse osmosis membranes and ultraviolet treatment are also potentially effective against VOC's and SOC's. Each of these technologies is discussed in the following paragraphs.

FIELD-TESTED TECHNOLOGIES

Carbon Adsorption

DWRD has been conducting extensive studies on the use of granular activated carbon (GAC) treatment with onsite regeneration for 10 years. Most of this research has been devoted to demonstrating the effectiveness of GAC for surface water treatment.[8] More recently, DWRD has been conducting studies that incorporate the use of carbon treatment for removal of VOC's and SOC's from groundwater. GAC is being studied for removing contaminants from groundwater at Suffolk County, New York, California's San Joaquin Valley, and Wausau, Wisconsin. Each of these projects is designed to examine a different aspect of GAC application and except for Wausau, they are intended to deal with the little-understood pesticide contamination problem.

In Suffolk County, the removal of organics and pesticides, and nitrates is being studied under various flow situations. Two parallel treatment systems (one consisting of GAC and ion exchange and the other consisting of reverse osmosis) are being operated at low flows similar to home usage. The costs for these two systems will be established along with unit operating efficiency so that a larger public water supply system can be designed and tested. The results from this study will be applicable to other areas, especially in farming communities, where multiple contamination of groundwater is identified.

The principle objectives of the San Joaquin Valley study are to (1) develop cost-effective design criteria for the removal of DBCP and other pesticides from water supplies by GAC, (2) to compare treatment methods other than GAC for the removal of these compounds, and (3) to improve and strengthen existing administrative guidelines and jurisdictional responsibilities pertain-

ing to both community water systems and private wells containing the compounds of interest. Pilot studies will be conducted with GAC, and results will be compared with those from existing operating systems. These comparisons should lead to recommendations for more effective design and operational criteria for GAC units used by water systems. The focus in this study will be on point-of-use GAC units that are now in use by small systems, individual homeowners, and farmers in the area. Disposal of treatment residues is also being studied.

The third site, in Wausau, Wisconsin, has multiple contaminants in its groundwater source from a nearby superfund site. GAC is the primary technology being studied, but air-stripping is being examined as a companion technology. The Wausau project is unique in that modeling techniques are being used to predict full-scale design criteria for a GAC plant. These predictions will be evaluated against the actual cost and performance associated with the building of GAC contactors onsite. The results from this study are expected to provide a useful methodology for extension to other GAC applications. The modeling techniques will be particularly useful in studying the long list of SOC's and VOC's that may be proposed for regulation under the current and future provisions of the Safe Drinking Water Act. In addition to modeling, minicolumn technology is also being studied. This methodology potentially allows investigators to acquire water from a given site and to study the performance of a small, high-pressure column in the presence of a natural water background. Results from these minicolumn experiments are expected to reproduce the breakthrough curve normally seen in pilot- and full-scale facilities.

Packed Tower

Aeration technology has proved to be especially effective for the removal of VOC's. However, the research at Wausau, Wisconsin (which also incorporates air stripping) indicates that aeration may in some cases be effective for removing compounds that have somewhat lower Henry's Law Constants than would normally expect to be removed by this process. The air-stripping at Wausau is being conducted in cooperation with the American Water Works Association Research Foundation. In this project, as with the carbon facilities, modeling is being used to predict the performance of packed-tower aeration. Results from this project are promising.

DWRD also has an air-stripping research project currently underway at Baldwin Park, California which is examining the removal of VOCs from a groundwater supply. As in Wausau, the Baldwin Park project is also examining the problems of off-gas control technology.

Another field-scale activity dealing with air-stripping has been concluded at Brewster, New York. In this project, modeling techniques and pilot-scale facilities were used to determine the scale-up relationships to be used for full-scale, air-stripping facilities. The purpose of the project was to develop a technique that could be used by consulting engineers to adequately predict the cost and performance of full-scale facilities using pilot aeration columns. Results from this project are promising.

PROMISING TECHNOLOGIES

Conventional Treatment

Conventional treatment is unlikely to be used for treating groundwater. However, field studies are being conducted at Tiffin, Ohio, where the river source contains periodically high concentrations of pesticides because of local

agricultural applications. Powdered activated carbon, added to the water normally treated only by conventional treatment, appears to be quite effective for removing synthetic organic chemicals.

Ozone Oxidation

Ozone oxidation is being studied extensively in DWRD's in-house pilot plant facilities.[10] Controlled pilot plant ozone treatment tests were conducted on 29 VOC's in distilled water and groundwater. Results showed that aromatic compounds, alkenes and certain pesticides are well removed by ozone treatment but that alkanes are poorly removed. Also, removal efficiency improved for the alkenes and aromatic compounds with increasing ozone dosage and for some alkanes with increasing pH. For most compounds, the efficacy of ozone was not affected by the background water matrix. Information from the literature concerning the ozone treatment of pure materials in the gaseous or liquid phase generally predicted the effectiveness of ozone in treating aqueous solutions.

Reverse Osmosis

Reverse osmosis (RO) has shown some promise in removing both VOC's and SOC's from groundwater.[11] Most of the efforts by DWRD to date have been on a pilot- or bench-scale basis, with some limited application of reverse osmosis for the removal of organics at the Suffolk County study mentioned previously. Primary indications are that certain RO membranes are very effective in removing a wide range of organic chemicals.

Ultraviolet Treatment

Ultraviolet light also shows some promise for removing organic contaminants, particularly when combined with ozone. DWRD is in the process of

funding a project with the Los Angeles Water and Power Company that deals with the removal of VOC's from groundwater using these two technologies. If successful, these chemicals will be oxidized to CO_2 and water, and the need to deal with off-gas control problems will be eliminated.

SECONDARY PROBLEMS

DWRD is very concerned that the technologies studied lead to no secondary problems. For example, while conducting GAC research on surface water supplies, it was discovered that dioxins were formed in the reactivation process. An extensive evaluation lead to the installation of an afterburner, which was found to eliminate these dioxin byproducts when operating at temperature of 2400°F.[12]

At Baldwin Park, California, the use of high-stack dispersion was investigated as a means of minimizing the impact of VOC removal from groundwater. At Baldwin Park and at Wausau, Wisconsin, gas-phase adsorption is being investigated for removal of both VOC's and SOC's from air stripping waste gases.

The project with the Los Angeles Water and Power Company is intended to investigate the water-phase oxidation of VOC's and SOC's to CO_2 and H_2O using ozone in combination with ultraviolet light. Gas-phase oxidation of VOC's and SOC's by ozone and ultraviolet light also appears promising.

Future work will concentrate on residuals control from various unit processes such as reverse osmosis.

COST AND PERFORMANCE

All of the field studies conducted by the DWRD include cost and performance as part of the data gathered for later evaluation and extrapolation to other conditions. In addition, as bench- and pilot-scale studies are conducted, cost estimates based on the development of cost equations and cost curves from previous studies are used to predict the most cost-effective technologies on which to concentrate scarce resources. Table 2 compares the costs and performance calculations for carbon adsorption, tower aeration, and diffused-air aeration for a selected set of VOC's.[13]

Some of the point-of-use technologies discussed in this paper, might best be managed by a centralized or circuit rider approach. In this case, the central authority would assume responsiblity for monitoring and maintaining the individual units installed on the homeowner's premises.

SUMMARY AND CONCLUSIONS

DWRD is responsible for evaluating the various types of technologies that might be used to meet the MCL's promulgated under the Safe Drinking Water Act. Because the source water for many utilities in the United States is groundwater, DWRD is especially concerned about conducting bench-, pilot- and field-scale studies on technologies that effectively treat groundwater. DWRD has research projects examining carbon adsorption and air stripping at the field-scale level as well as ozone oxidation, ultraviolet light, and reverse osmosis on the bench and pilot scales. Table 3, summarizes the various technologies examined, and based on data gathered to date, it attempts

to characterize their relative performances on both Phase I and Phase II organics.

Although Table 3 only provides a general guideline for removal of compounds, nevertheless several interesting trends are noted. Carbon adsorption appears to provide removal for a wide range of organics whereas conventional treatment is revealed as a poor treatment for those compounds listed in the table. Packed tower aeration manifests itself as an excellent technology for volatile organic compounds and may have application for a limited number of pesticides. Ozone oxidation comes to light as a good treatment technology for certain classes of organics such as simple alkenes and aromatics, as well as certain similar, but more complex organic structures. In regard to reverse osmosis, although only a few organics have been subjected to long-term testing, promising removals for several low molecular weight organics can be seen.

Table 3 was generated using a variety of sources, including EPA-DWRD pilot- and field-scale studies, Henry's Law Constants for prediction of removal of some of the pesticides, as well as the use of oxidative trends for predicting the removal of complex pesticides. This table therefore carries the caveat that the cited removals should not be used for design purposes, but that each technology must be tested on compounds, under field conditions, before the EPA-DWRD will advocate a technology's use.

Nevertheless, given the widespread nature of groundwater contamination these technological evaluations should be highly useful to EPA's regulatory process and to consultants, state officials, and individual communities as well.

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TABLE 1. TREATMENT TECHNOLOGIES FOR REMOVING SOC's AND VOC's

Technology Status	Technology Description	Contaminants for which Technology is Best Suited
Field tested technologies	Carbon adsorption	VOC's & SOC's
	Packed tower and Diffused-air aeration	VOC's
Promising technologies	Conventional treatment	SOC's
	Ozone oxidation	VOC's & SOC's
	Reverse osmosis	VOC's & SOC's
	Ultraviolet treatment	VOC's & SOC's

TABLE 2. COST SUMMARY FOR SELECTED VOC's[13]

VOC	Capacity mgd[+]	Capacity ug/L	Percent removal	Cost, $/thousand gal[†] Tower aeration	Diffused-air aeration	Carbon adsorption
Trichloro-ethylene	0.5	100	90	0.273	0.546	0.868
		10	99	0.287	0.793	0.918
		1	99.9	0.296	1.032	1.010
		0.1	99.99	0.303	1.270	1.124
	1	100	90	0.182	0.383	0.637
		10	99	0.191	0.611	0.679
		1	99.9	0.196	0.850	0.765
		0.1	99.99	0.202	1.088	0.867
	10	100	90	0.083	0.207	0.356
		10	99	0.088	0.403	0.390
		1	99.9	0.093	0.587	0.458
		0.1	99.99	0.099	0.755	0.543
Tetrachloro-ethylene	0.5	100	90	0.279	0.637	0.610
		10	99	0.293	0.935	0.660
		1	99.9	0.302	1.228	0.705
		0.1	99.99	0.308	1.486	0.805
	1	100	90	0.186	0.460	0.453
		10	99	0.194	1.752	0.502
		1	99.9	0.201	1.046	0.548
		0.0	99.99	0.206	1.296	0.651
	10	100	90	0.085	0.277	0.197
		10	99	0.091	0.514	0.224
		1	99.9	0.098	0.726	0.251
		0.1	99.99	0.103	0.905	0.313
1,1,1-Tri-chloro-ethane	0.5	100	90	0.270	0.502	1.445
		10	99	0.289	0.825	1.651
		1	99.9	0.307	1.421	1.945
		0.1	99.99	0.332	2.572	2.605
	1	100	90	0.180	0.348	1.396
		10	99	0.192	0.644	1.500
		1	99.9	0.205	1.234	1.801
		0.1	99.99	0.230	2.313	2.402
	10	100	90	0.082	0.176	0.802
		10	99	0.089	0.430	0.973
		1	99.9	0.102	0.860	1.229
		0.1	99.99	0.122	1.821	1.818
Carbon tetra-chloride	0.5	100	90	0.264	0.428	0.942
		10	99	0.287	0.531	1.021
		1	99.9	0.272	0.600	1.132
		0.1	99.99	0.280	0.648	1.340
	1	100	90	0.176	0.292	0.703
		10	99	0.181	0.371	0.775
		1	99.9	0.184	0.427	0.940
		0.1	99.99	0.186	0.470	1.063
	10	100	90	0.081	0.133	0.408
		10	99	0.083	0.196	0.467
		1	99.9	0.084	0.247	0.550
		0.1	99.99	0.085	0.286	0.719

(See footnotes at end of table)

(Continued)

TABLE 2. COST SUMMARY FOR SELECTED VOC's[13] (Contd.)

VOC	Capacity mgd[+]	Capacity ug/L	Percent removal	Cost, $/thousand gal[†] Tower Aeration	Diffused air aeration	Carbon adsorption
Cis-1,2-Dichloro-ethylene	0.5	100	90	0.284	0.727	2.513
		10	99	0.296	1.010	2.791
		1	99.9	0.304	1.281	3.153
		0.1	99.99	0.310	1.572	3.511
	1	100	90	0.189	0.547	2.156
		10	99	0.196	0.828	2.417
		1	99.9	0.202	1.098	2.760
		0.1	99.99	0.208	1.379	3.099
	10	100	90	0.087	0.350	1.735
		10	99	0.093	0.571	1.989
		1	99.9	0.099	0.763	2.327
		0.1	99.99	0.104	0.966	2.660
1,2-Dichloro-ethane	0.5	100	90	0.276	0.587	1.286
		10	99	0.285	0.749	1.465
		1	99.9	0.292	0.901	1.748
		0.1	99.99	0.297	1.054	2.322
	1	100	90	0.184	0.415	1.015
		10	99	0.190	0.568	1.177
		1	99.9	0.194	0.720	1.437
		0.1	99.99	0.197	0.871	2.980
	10	100	90	0.084	0.237	0.675
		10	99	0.087	0.368	0.820
		1	99.9	0.090	0.489	1.057
		0.1	99.99	0.094	0.603	1.566
1,1-Dichloro-ethylene	0.5	100	90	0.262	0.406	0.880
		10	99	0.265	0.448	0.963
		1	99.9	0.270	0.500	1.066
		0.1	99.99	0.272	0.531	1.243
	1	100	90	0.174	0.274	0.647
		10	99	0.177	0.307	0.721
		1	99.9	0.180	0.348	0.814
		0.1	99.99	0.181	0.371	0.977
	10	100	90	0.080	0.121	0.364
		10	99	0.081	0.144	0.423
		1	99.9	0.082	0.176	0.499
		0.1	99.99	0.083	0.196	0.640

[+]To convert from mgd to m^3/day, multiply by 3,785.
[†]To convert from $/1,000 gal to $/$m^3$, multiply by 0.26412

TABLE 3. PERFORMANCE SUMMARY FOR TECHNOLOGIES EXAMINED

Regulatory Phase	Organic Compounds	REMOVAL EFFICIENCY† Granular Activated Carbon Adsorption Filtrasorb 400[a]	Packed Tower Aeration	Reverse Osmosis Thin Film Composite	Ozone Oxidation (2-6 ppm)	Conventional Treatment
	VOLATILE ORGANIC CONTAMINANTS					
	Alkanes					
I	Carbon Tetrachloride	●	●	●	0	0
I	1,2-Dichloroethane	●	●	●	0	0
I	1,1,1-Trichloroethane	●	●	●	0	0
II	1,2-Dichloropropane	●	●	●	0	0
II	Ethylene Dibromide	●	●	●	0	0
II	Dibromochloropropane	●	●	NA	0	0
	Alkenes					
I	Vinyl Chloride	●	●	NA	●	0
II	Styrene	NA	NA	NA	●	0
I	1,1-Dichloroethylene	●	●	NA	●	0
II	cis-1,2-Dichloroethylene	●	●	0	●	0
II	trans-1,2-Dichloroethylene	●	●	NA	●	0
I	Trichloroethylene	●	●	●	●	0
	Aromatics					
I	Benzene	●	●	0	●	0
II	Toluene	●	●	NA	●	0
II	Xylenes	●	●	NA	●	0
II	Ethylbenzene	●	●	0	●	0
II	Chlorobenzene	●	●	●	●	0
II	o-Dichlorobenzene	●	●	●	●	0
I	p-Dichlorobenzene	●	●	NA	●	0
	PESTICIDES					
II	Pentachlorophenol	●	0	NA	●	NA
II	2,4-D	●	0	NA	●	0
II	Alachlor	●	●	●	●	0
II	Aldicarb	NA	0	NA	NA	NA
II	Carbofuran	●	0	●	●	0
II	Lindane	●	0	NA	0	0
II	Toxaphene	●	●	NA	NA	0
II	Heptachlor	●	●	NA	●	NA
II	Chlordane	●	0	NA	NA	NA
II	2,4,5-TP	●	NA	NA	●	NA
II	Methoxychlor	●	NA	NA	NA	NA

(See footnotes at end of table) (Continued)

TABLE 3. PERFORMANCE SUMMARY FOR TECHNOLOGIES EXAMINED (Contd.)

Regulatory Phase	Organic Compounds	REMOVAL EFFICIENCY† Granular Activated Carbon Adsorption Filtrasorb 400[a]	Packed Tower Aeration	Reverse Osmosis Thin Film Composite	Ozone Oxidation (2-6 ppm)	Conventional Treatment
	OTHER					
II	Acrylamide	NA	0	NA	NA	NA
II	Epichlorohydrin	NA	0	NA	0	NA
II	PCB's	●	●	NA	NA	NA

†● = Excellent 70% - 100%
● = Average Removal 30% - 69%
0 = Poor 0% - 29%
NA = Data not available or compound has not been tested by EPA Drinking Water Research Division
a = Excellent removal category for carbon indicates compound has been demonstrated to be adsorbable onto GAC, in full- or pilot-scale applications, or in the laboratory with characteristics suggesting GAC can be a cost-effective technology.